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Micro-Raman study of the spin and orbital ordering in $SmVO_3$

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Abstract. The spin and orbital ordering have been examined for high-quality $SmVO_3$ polycrystalline compound using Raman spectroscopy. Measurements were obtained on individual microcrystallites in the approximate $y(zz)\bar{y}$ and $y(xx)\bar{y}$ scattering configurations at low temperatures (down to 20K). Based on our experimental data we present evidence of a coexistence of the G and C-type OO phases that occur in $SmVO_3$ for temperatures below 100K. This phase coexistence of orbital orderings puts $SmVO_3$ in a different category from all the other RVO_3 compounds that have been studied yet.

1. Introduction

$SmVO_3$ is a perovskite-type vanadate of the form RVO_3 (R=rear earth or Y) with medium size R-cation. The up to now experimental investigations have not defined clearly its phase diagram [1, 2, 3]. The first structural phase transition of $SmVO_3$ occurs at T_{OO1}=200K [1, 4]. At this temperature the symmetry of the lattice changes from orthorhombic Pbnm to monoclinic $P2_1/c$ accompanied concomitantly with the G-type orbital ordering (OO), as temperature is lowered. The second transition occurs at $T_N \simeq 129$K [1, 2, 4] where the system undergoes a magnetic transition from paramagnetic to C-type (SO) antiferromagnetic phase. According to Blake *et al* [1] $SmVO_3$ undergoes a third transition at T_{OO2}=115K, which leads to the coexistence of the G and C-type OO phases.

Raman spectroscopy can be used for the investigation of OO because of the sensitivity of this technique to lattice distortions that in the particular case are caused by the Jahn-Teller effect. In this work the temperature dependence of the modes observed in $SmVO_3$ is investigated in order to clear out the situation with the phase transitions that occur in this system.

2. Experimental setup

Polycrystalline compound of high-quality $SmVO_3$ has been examined using Raman spectroscopy. The Raman spectra were obtained at nominal temperatures of 20K to RT with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid nitrogen charged coupled device (CCD) and a microscope (magnification x100). The 514.5 nm line of an Ar^+ laser was used for excitation. Low temperature measurements were achieved using an Oxford micro-He cryostat appropriately modified to allow the study of microcrystallites at various scattering geometries. The spectra

presented here have been acquired on individual microcrystals (typical size of a few μm) in the zz and xx/yy polarization. Accumulation time were of the order of 3-6 hours.

3. Results and Discussion

Figs.1 and 2 present Raman spectra in the $y(zz)\bar{y}$ and $y(xx)\bar{y}$ (or $x(yy)\bar{x}$) scattering polarization respectively, at various temperatures for $SmVO_3$. The $y(zz)\bar{y}$ polarization spectra at RT are

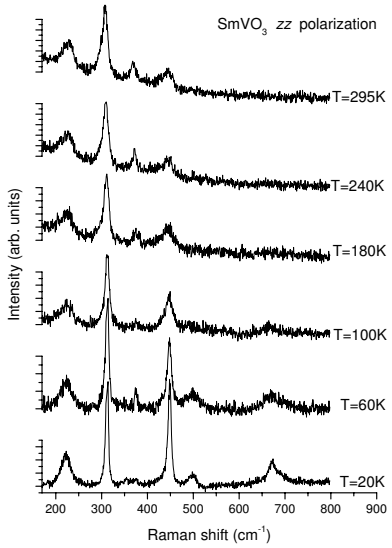

Figure 1. Typical Raman spectra for selected temperatures in the $y(zz)\bar{y}$ scattering geometry.

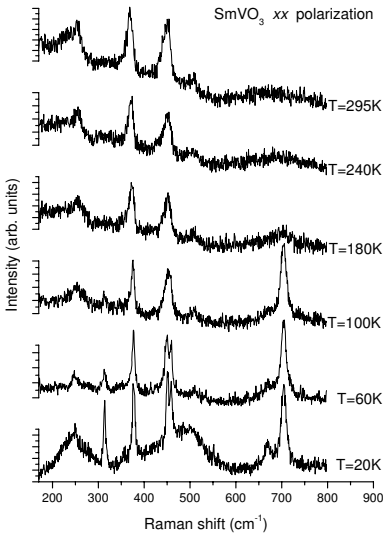

Figure 2. Typical Raman spectra for selected temperatures in the $y(xx)\bar{y}$ scattering geometry.

characterized by three modes that appear at $\sim$226 cm^{-1}, $\sim$308 cm^{-1} and $\sim$442 cm^{-1}. Miyasaka *et al*, investigated the Raman spectra of other pervoskite-type RVO_3 (R=La, Nd, and Y) compounds and observed similar peaks, the energy of which decreases as the ionic radii increases from Y to La [4]. Considering the ionic radii of Sm the relative modes are expected to appear very close to those observed in our spectra (242, 313 and 452 cm^{-1}, respectively). Therefore, these bands share the same origin with those observed for the other RVO_3 compounds. Based on this assignment the band appearing at $\sim$226 cm^{-1} is the rotation of the VO_6 octaedra, while the other two modes are assigned as oxygen bending and Jahn-Teller mode, respectively [4, 5]. However, according to the proposal of Iliev *et al* for the isostructural $RMnO_3$ compounds a different assignment is suggested for the last two modes [6]. The mode appearing at $\sim$308 cm^{-1} is related to the vibrations of the O1 atoms, while the one appearing at $\sim$442 cm^{-1} has been assigned to the out of phase bending A_g phonon. Furthermore, based on the assignment of Sugai *et al* for YVO_3, the mode at $\sim$308 cm^{-1} is related with R-O1 mixed vibrations [7]. However, this mode, as mentioned before, follows very well the dependence of the size of R cation and not the mass harmonic law. Therefore the above assignment is rather impossible.

At low temperatures two extra peaks appear in the Raman spectra at $\sim$497 cm^{-1} and $\sim$670 cm^{-1}. The energy of both peaks remains almost unchanged until 80K while a decrease of $\sim$5 cm^{-1} and $\sim$7 cm^{-1}, respectively is observed at T=100K. For higher temperatures both of these modes disappear. The normalized intensity of the lower energy mode shows a maximum at 40K and then decreases with increasing temperature (Fig.3a). A systematic decrease of intensity is

also observed for the mode appearing at ∼670 cm^{-1} (Fig.3b). The extrapolation of a second order polynomial fit of the intensity of the first peak indicates that the band disappears at nominal temperature of ≃120K, very close to T_N=129K (the difference from 129K is due to the local heating of the sample from the laser beam). This denotes that the peak at ∼497 cm^{-1} is related to the magnetic transition from paramagnetic to C-type antiferromagnetic phase.

The peak at ∼497 cm^{-1} also appears in the Raman spectra for other RVO_3 compounds, while its energy remains unchanged and independent of R [4]. According to the analysis of Miyasaka *et al* this mode is assigned as two orbiton excitations [4, 5]. However, Raman measurements on other perovskite-like compounds show a peak in the same energy region, being almost independent of R, which has been assigned as a Jahn-Teller phonon [7, 8].

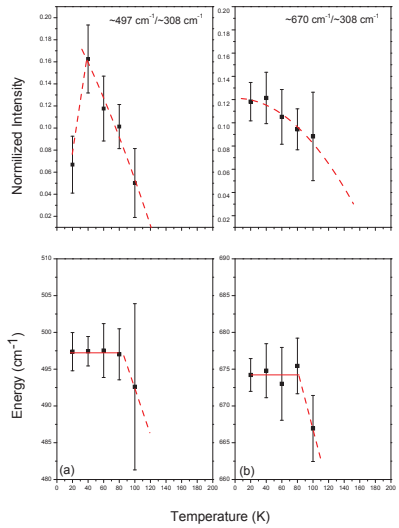

Figure 3. Temperature dependence of the energy and intensity of the ∼497 cm^{-1} (a) and ∼670 cm^{-1} (b) modes.

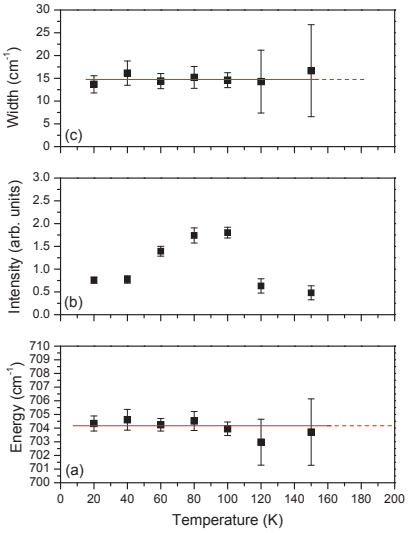

Figure 4. Temperature dependence of the energy (a), intensity (b) and width (c) of the ∼704 cm^{-1} mode.

In the *xx* polarization spectra at RT there are two characteristic modes appearing at ∼368 cm^{-1} and ∼449 cm^{-1}. The first one is observed only in the Raman spectra of $SmVO_3$ and $NdVO_3$ [4] and compared it with other perovskites it is possible to be related with oxygen bending vibrations. The peak at ∼449 cm^{-1} has an asymmetric shape but the asymmetry is reduced with decreasing temperature and below 80K two peaks at ∼450 cm^{-1} and ∼459 cm^{-1} are clearly observed. Therefore we believe that there are two modes appearing in the *xx* Raman spectra at this energy region but the lower frequency one progressively disappears with increasing temperature leading to the apparent asymmetric shape of the higher energy peak.

Additionally, two broad bands at ∼250 cm^{-1} and ∼503 cm^{-1} appear at all temperatures studied. The first peak has an asymmetric tail (Fano shape) and based on the assignment for the $RMnO_3$ compounds it can be related with the octahedral tilting angle. The second one is very weak and it is possible to be the second order Raman scattering of the band appearing at ∼250 cm^{-1}, since its energy is about twice the energy of the Fano shaped one.

For temperatures below 180K an additional peak at ∼704 cm^{-1} is observed in the *xx* polarization spectra. The intensity of this mode strongly increases with decreasing temperature, reaches a maximum at 100K and then decreases again, but it is still observed as a strong peak

down to T=20K (Fig.4). At T=100K another extra peak appears in the *xx* polarization Raman spectra at ∼670 cm^{-1} and is still observed down to T=20K with increasing intensity.

The peak at ∼704 cm^{-1} has also been observed for other perovskite-like RVO_3 (R=rear earth or Y) compounds with increasing energy as the ionic radius increases from Y to La [4, 9]. In all cases this band starts appearing for temperatures below T_{OO1} and therefore it has been connected with the orthorhombic to monoclinic transition accompanied concomitantly with the G-type OO [4, 5, 9]. The appearance of this mode for low temperatures (down to 20K), as shown in Figure 2, indicates that $SmVO_3$ remains monoclinic at least until this temperature.

For temperatures below 100K the ∼704 cm^{-1} band is accompanied with another peak at ∼670 cm^{-1}, which is still observed down to T=20K. This new mode has also been observed in YVO_3 [4, 7] and $Y_{1-x}Ca_xVO_3$ [10] and assigned to an oxygen stretching mode. In both cases the mode at ∼670 cm^{-1} appears for temperatures below T_{OO2} where a second phase transition from monoclinic to orthorhombic symmetry occurs in the system, while no sign of it has been observed for compounds with monoclinic symmetry at low temperatures [4]. For that reason it is connected with the C-type OO and the orthorhombic phase. In such a case, the coexistence of this mode with the one related with the G-type OO phase for temperatures below 100K, is an evidence that even though at low temperatures the monoclinic phase and the G type OO dominate in $SmVO_3$, in the specific temperature region the orbital ordering is not clear and a coexistence of the G and C-type OO is observed. This is in agreement with the results of ref. [1] in which it was observed, based on high resolution x-ray powder diffraction experiments, a coexistence of phases below 115K with monoclinic and orthorhombic symmetries until 5K.

4. Conclusions

In this work the temperature dependence of the modes appearing in the *zz* and *xx* Raman spectra of $SmVO_3$ is investigated in order to examine the possible relation between them and the phase transitions that occur in the compound. We found out that at low temperatures three extra peaks at ∼497 cm^{-1}, ∼670 cm^{-1} and ∼704 cm^{-1} appear in the Raman spectra, related with the C-type SO, C-type OO and G-type OO, respectively. The modes at ∼497 cm^{-1} and ∼704 cm^{-1} increase in intensity with decreasing temperature indicating that below T_N the G-type OO coexists with the C-type SO phase. Finally, the appearance of a peak for temperatures below 100K related with the C-type OO additionally with the one connected with the G-type OO denotes the coexistence of the G and C-type orbital ordered phases in $SmVO_3$.

Acknowledgments

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